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Quartz crystal microbalance device for electronic nose application

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Quartz crystal microbalance technology was developed for measurement of a tiny amount of mass put on the sensor in a form of thin layer. Since then many other applications were developed, including measurement in liquid phase, sorption etc..
The main idea is to measure frequency and other parameters of vibrating quartz crystal as dependent on the amount and properties of thin layer of cover material. The quartz crystal vibration frequency in a resonant mode is very stable. Utilizing this property one can easily measure influence of external mass addition of an order of below 1ng/cm^2. The dependence of frequency on mass adsorbed on the crystal is linear and is given by the equation:

$$\Delta f = -k \times \Delta m$$

Where: Δf is the frequency change due to the sorption of mass Δm on the vibrating surface of the crystal.
Measurement mass difference is of an order of nano grams per square centimeter and can reach sensitivity below of one particle layer of an adsorbed material.
This sensitivity allows to measure sorption of air pollutants that are diluted in the ambient air, like odorant substances, in low concentrations.
In the paper some technical details of QCM will be described. The device is based on modern technology of digital data synthesis (DDS) that allows to generate the stable and robust frequency with high precision. The technology allows to scan frequency properties of the QCM sensor and draw conclusions on the reactance change during the measurement. This together with the application of data analysis leads to a method of more detail knowledge of adsorbed layer properties. The DDS technology opens some possibilities for developing of electronic nose devices with enhanced sensitivity and lower price.
Multi sensor technology allows the application of neural network analysis of the measurement results.

1. QCM basics

Quartz crystal microbalance bases on application of vibrating crystal as a sorbed mass sensor. It may be applied to measure sorption out of gaseous environment as well as from liquid environment. Due to a mass added to the sensor surface the frequency of quartz crystal vibration changes what can be measured provided the sensible frequency meter is available.

Another way to discover the mass addition to the quartz surface or eventually vibration properties of the ambient is to measure the whole impedance curve in function of frequency of exciting current. The first method is called active because the frequency of the quartz is a mayor factor that drives vibrating system the second is called passive because quartz is driven by an independent, variable frequency generator, and properties of quartz are scanned for variable frequence (Talib et al. 2006).
QCM sensors are build of thin plate of quartz crystal with metal electrodes on each side of a plate. Metal electrodes are used to provide electrical excitation of quartz crystal. It is a sensitive device mostly due to the intrinsic stability of quartz vibrator itself. Any external factor that influences the quartz vibration may be easily measured. For example it may measure sorbed masses with the accuracy of about 1ng per square centimeter.

Till now QCM technology was developed to measure various effects like:

- measurement of mass adsorbed on a crystal
- electrolytic metal deposition
- vacuum metal vapour deposition
- corrosion process
- anodic metal oxidation
- electrosorption of large particles like protein
- polymerisation process
- ultra thin layers monitoring.

Assuming the simplest behaviour of deposited layer as a merely mass added to the vibrating system Sauerbray (1957) come to the conclusion that the quartz frequency will change according to the equation:

$$\Delta f = \frac{-2 f_{ro}^2}{A\sqrt{\rho_q G_q}} \Delta m_q$$

Where: Δf is the frequency change due to addition of mass Δm_q onto the vibrating quartz surface area A , with the resonant frequency f_{ro}, $\rho_q = 2.648\, g\, cm^{-3}$ is quartz density and $G_q = 2{,}947 \mathrm{x} 10^{11}$ g cm^{-1} s^{-2} is its shear modulus.

When one considers also vibration properties of the adsorbed layer will come to different equation of vibrating quartz behaviour. In such a case more complex analysis is needed to interprete the frequency dependent impedance of the quartz crystal togeter with dragged to vibrate environment (Vogt et al. 2004). Measurement of these properties need to be done by scanning of the quartz impedance with variable frequency, and measure shift angle between the current and voltage for the frequency range. Careful interpretation of the results of such measurement in terms of proposed theory leads to the assessment of certain properties of the measured system.

Together with the sensor vibrating properties, other parameters can be controlled and measured like temperature, optical properties of the quartz surface, relative humidity of ambient gas etc., this allows to widen the amount of information gathered during measurement (Tenan 1998).

2. Direct Digital Synthesis

Direct Digital Synthesis (DDS) is a new technology for frequency generation which underwent fast development last years. DDS method of frequency generation is often used instead of Phase Locked Loop (PLL) technology basically due to shorter time of reaction on switch of the output frequency. In DDS synthesizers the output signal is completely digitally generated and controlled according to the frequency, phase and amplitude. It is allowed by the application of Digital to Analog Converter as an output device fed from the carefully calculated digital input. As todays digital processors can work with the clock frequency of an order of GHz, the otput DAC control word can be changed with similar frequency. Development of integrated circuit form of DDS generators allows easy and relatively cheap application for certain measurement purposes. In this paper an idea of DDS application for measurement of QCM for odour assessment.

3. DDS QCM idea

The quartz sensor in proposed QCM construction is driven by the DDS frequency generator with the possibility to vary frequency and amplitude of the signal in the wide range. After amplification the voltage generated on the sensor cristal is compared wit the incident signal by the phase detector giving the information about the phase shift due to impedance change of the cristal. In the construction the DDS generator allows to generate four signals independently and drive up to four cristals at the same time with independently set frequencies and phases of signals. Measurement of phase signal and control of the whole device is performed by the microcontroller programmed especially for that task. The whole measurement process and the data collection is done by the PC computer with the USB port. In a case of olfactory sensing more sensors are needed. It may be done by electrical coupling of two or more DDS chips thus providing the synchronous action of all quartz sensors.

4. DDS QCM construction

In the proposed device (Fig. 1) we apply the microcontroller Aduc847 with multiplexed ten channel analog input for the 24 bit analog to digital converter. It provides also analog output and number of digital input and output lines to control the device. Microcontroller can store quite complicated control program in its on chip program memory of 62kB.

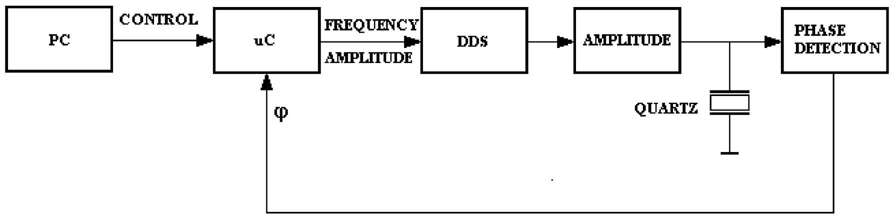

Fig.1 Device schematic idea

The microcontroller controlls DDS chips with four channels of independent output each with the serial port, here we use Analog Devices AD9959 chips for this purpose. With the internal clock of maximum 500MHz they allow to generate clean sinusoidal signal in a range 6-20MHz. They allow to control the output amplitude also in a digital manner. Output DAC offers 10 bits resolution. Additionally there is a possibility to diminish the output signal by a factor of 4. Wit this kind of generator the application of quartz monitors with base frequency 6MHz and 10MHz without any change of the schematic just with changing control word of the DDS generator is possible. The signal from the DDS generator is filtered with the low pass filter in order to filter out higher order overtones from the main sinusoidal signal. After that the signal is amplified with the amplifier – buffer. Quartz crystals are fed with the application of circuit similar to that published in Hayderer at al. (1999). The phase detector applied is based on the Analog Devices circuit AD834 which allows high precision measurement of the phase shift between input signals in the range 0-300MHz. The prototype test construction was built with the application of evaluation board presented at figure 2.

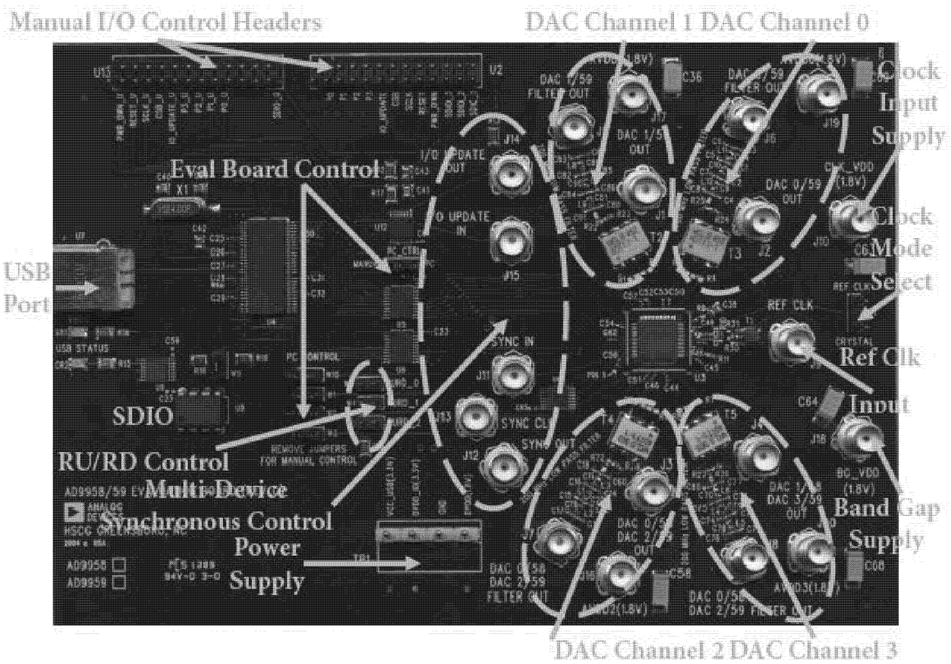

Fig.2 DDS evaluation board

5. Summary

Presented construction allows to drive an array of QCMs at the same time, with the frequency specific for each QCM. It allows the scan of the impedance properties of each QCM sensor with respect to its resonant frequency. It allows to plan measurement independently for each QCM in the array due to possibility to drive each quartz sensor with separate frequency and phase shift. Because of this even each quartz can have specific resonant frequency in the range 6 – 20MHz. It also allows to drive 6MHz quartz with its third overtone. The main application of the presented device is the measurement of air pollution with chemicals highly olfactory active. Multi sensor device with proper activation of the sensors will allow to discover air pollution allowing the construction to act as the electronic nose. Further application of neural network algorithm for data interpretation will allow to discover specific odour components. Due to the stability of the quartz frequency, the device can monitor the air pollution for long time. Collected data can be applied for assessment of mean air pollution concentration.

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